

THE INVESTIGATION OF CHLORATES AS A POSSIBLE SOURCE OF OXYGEN AND CHLORINE DETECTED BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT IN GALE CRATER, MARS. B. Sutter^{1,2}, P.D. Archer^{1,2}, D.W. Ming², P.B. Niles², J.L. Eigenbrode³, H. Franz³, D. P. Glavin³, A.C. McAdam³, P. Mahaffy³, J.C. Stern³, R. Navarro-Gonzalez⁴, C.P. McKay⁵. ¹Jacobs, Houston, TX 77058, ²NASA Johnson Space Center, Houston TX 77058, ³NASA Goddard Space Flight Center, Greenbelt, MD 20771, ⁴Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, ⁵NASA Ames Research Center, Moffett Field, CA 94035.

Introduction: The Sample Analysis at Mars (SAM) instrument onboard the Curiosity rover detected O₂ and HCl gas releases from the Rocknest (RN) eolian bedform and the John Klein (JK) and Cumberland (CB) drill hole materials in Gale Crater (Fig. 1) [1,2]. Chlorinated hydrocarbons have also been detected by the SAM quadrupole mass spectrometer (QMS) and gas chromatography/mass spectrometer (GCMS) [1,2,3,4]. These detections along with the detection of perchlorate (ClO₄⁻) by the Mars Phoenix Lander's Wet Chemistry Laboratory (WCL) [5] suggesting perchlorate is a possible candidate for evolved O₂ and chlorine species. Laboratory thermal analysis of perchlorates has yet to provide an unequivocal temperature match to the SAM O₂ and HCl release data [1,2]. Iron mineralogy found in the Rocknest materials when mixed with Ca-perchlorate does cause O₂ release temperatures to be closer match to the SAM O₂ release data but more work is required in evaluating the catalytic effects of Fe mineralogy on perchlorate decomposition [6]. Chlorates (ClO₃⁻) are relevant Mars materials and potential O₂ and Cl sources [7,8]. The objective of this work is to evaluate the thermal decomposition of select chlorate (ClO₃⁻) salts as possible sources of the O₂ and HCl releases in the Gale Crater materials.

Materials and Methods: The Rocknest material examined by SAM consists of unconsolidated sand and dusty material [1]. John Klein and CB are drill hole samples (~6 cm deep) derived from the Sheepbed mudstone and are 3 m and 10cm apart, horizontally and vertically, respectively [2]. The < 150 μ m size fraction was examined by SAM. Samples were heated (35 $^{\circ}$ C min⁻¹) from 35 to ~840 $^{\circ}$ C in a 30 mb He purge at ~0.8 sccm. Evolved gases were analyzed by the SAM-QMS over the entire temperature range.

A laboratory Setaram Sensys-Evo differential scanning calorimeter (DSC) coupled to a Stanford Research Systems Universal Gas Analyzer at Johnson Space Center (JSC) were configured to operate similarly to the SAM oven/QMS system. Samples are heated from 25 to 730 $^{\circ}$ C under flowing He (3 ml/min) at 30 mb total pressure. Reagent grade (Sigma-Aldrich) NaClO₃ \cdot H₂O and KClO₃ \cdot H₂O were used for this work. Mg(ClO₃)₂ \cdot nH₂O, and Ca(ClO₃)₂ \cdot nH₂O were synthesized by combining dissolved reagent BaClO₃ \cdot H₂O in water and with equal molar dissolved reagent MgSO₄ and CaSO₄, respectively. Precipitated BaSO₄ was cen-

trifuged out. The remaining solution was boiled down to ~20 ml and then frozen and subsequently freeze-dried to allow for Ca- and Mg-chlorate precipitation. Chlorate synthesis was verified by X-ray diffraction.

Results and Discussion: The O₂ peak temperatures are ~315 and 385 $^{\circ}$ C for CB and RN, respectively (Fig. 1) suggesting differing O₂ producing species for each material. John Klein has two O₂ peaks at ~225 and 370 $^{\circ}$ C (Fig. 1) which suggests the presence of two O₂ evolving species, consumption of O₂ during organic combustion, or thermal oxidation of a ferrous phase (e.g., magnetite to maghemite transition) [2].

The HCl temperature release characteristics from CB were different than JK and RN. Cumberland was marked by two HCl peaks at ~350 and ~730 $^{\circ}$ C, while RN and JK possessed a gradual HCl release that peaked near ~760 $^{\circ}$ C (Fig. 2). The first HCl phase in CB is coincident with the O₂ release indicating that HCl is sourced from an oxychlorine species like perchlorate or chloride (Figs. 1,2) [2]. The second CB HCl peak and John Klein and RN peak HCl releases do not coincide with peak O₂ releases.

The O₂ release peak temperatures for Ca-chlorate and Mg-chlorate are the closest match to the RN and second JK O₂ peaks (Fig. 1). The Mg-chlorate O₂ peak nearly coincides with RN and second JK O₂ peaks while the Ca-chlorate O₂ peak are ~25 to 40 $^{\circ}$ C higher than the RN and JK peaks, respectively. The Na-chlorate and K-chlorate O₂ peaks are higher than all the O₂ peak temperatures for RN, JK, and CB (Fig. 1).

None of the chlorates evaluated here coincide with the CB and first JK O₂ peaks (Fig. 1). Iron-chlorate has yet to be evaluated and may yield O₂ peak temperatures consistent with CB and the first JK O₂ peaks.

The Mg-chlorate HCl peak is closest to the CB HCl peak 1 but does not yield any HCl that could explain the high temperature (>700 $^{\circ}$ C) HCl peaks in RN, JK, or CB (Fig. 2). The HCl evolution is caused by Mg-chlorate decomposition to MgO which liberates Cl₂ that reacts with water to form HCl as indicated by heated stage X-ray diffraction (data not shown). The Mg-chlorate peak HCl release temperature is near (within 25 $^{\circ}$ C) to the CB5 peak 1 HCl release. This suggests that Mg-chlorate could be a reasonable candidate for explaining the CB HCl peak 1. The Mg-chlorate O₂ release; however, does not provide an ideal match

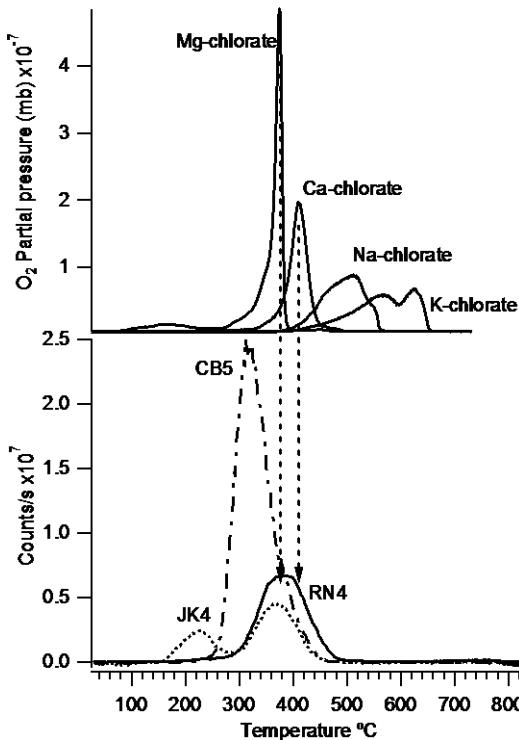


Fig. 1. Oxygen release versus temperature from Rocknest-4 (RN4), John Klein-4 (JK4) and Cumberland-5 (CB5) materials as measured by the SAM-QMS and select chlorate salts analyzed by the JSC-SAM testbed. JK4 is multiplied $\times 5$ relative to RN4 and CB5. Arrowed dotted lines indicate Mg- and Ca-chlorate O_2 peak positions relative to O_2 releases in the Gale Crater materials.

to the CB O_2 peak (Fig. 1) suggesting that Mg-chlorate may not be a candidate for CB.

There are two minor HCl releases just above baseline from Ca-chlorate at 70°C and 400°C (Fig. 2). The 400°C release is related to Ca-chlorate decomposition but the low temperature release may be attributed to a temporary HCl baseline rise caused by significant water release associated Ca-chlorate dehydration (data not shown). Much less HCl is produced from Ca-chlorate decomposition because most of the Cl combines with Ca to form $CaCl_2$. No HCl releases were detected for Na- and K-chlorate because all Cl is used to form $NaCl$ and KCl [9]. Above 450°C, the Ca-chlorate HCl baseline levels appear to rise slightly which is similar to the observed HCl baseline rise in RN and JK (Fig. 2). The DSC maximum temperature is 730°C and it is unknown if the baseline would have risen and peaked, similar to what was observed for RN and JK. Nevertheless, the Ca-chlorate HCl baseline rise at high temperature coupled with the close O_2 release temperature match to RN and JK suggests that Ca-chlorate may be

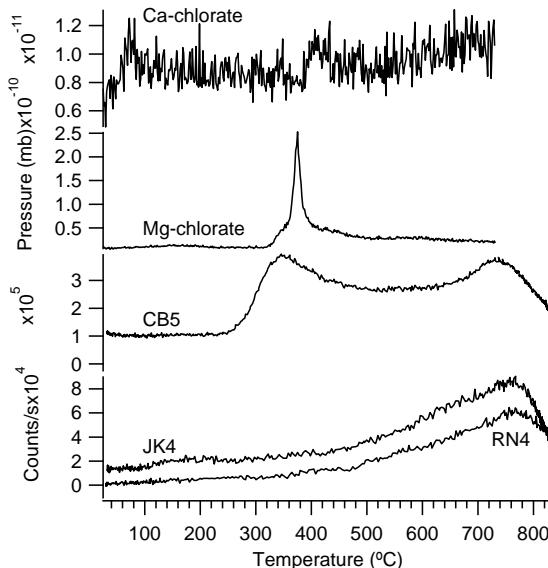


Fig. 2. Hydrochloric acid (mass 36) release versus temperature from Rocknest-4 (RN4), John Klein-4 (JK4) and Cumberland-5 (CB5) materials as measured by the SAM-QMS and select chlorate salts analyzed by the JSC-SAM testbed.

a candidate oxychlorine species for RN and JK.

No chlorates matched O_2 releases for JK peak 1 and CB. Mg-chlorate O_2 release temperature is consistent with RN and JK but does not have a matching HCl release. Ca-chlorate O_2 and HCl release characteristics are both close with RN and JK (O_2 peak 2) which suggests that Ca-chlorate may be a better candidate oxychlorine species than Mg-chlorate. The thermal decomposition of Fe(II)- and Fe(III)-chlorate will be evaluated next to determine if these chlorate species can better explain the O_2 and HCl release characteristics of RN, JK and/or CB. Mixing iron phases (e.g., hematite) with chlorates are known to have catalytic effects that cause chlorate O_2 and HCl release temperatures to differ from pure chlorate phases [9]. Future work will mix iron phases (e.g., hematite, magnetite, pyrite, fayalite, amorphous Fe material) known to occur in RN, JK, and CB with chlorates to determine if improved O_2 and HCl release temperature matches with the Gale materials can be obtained.

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